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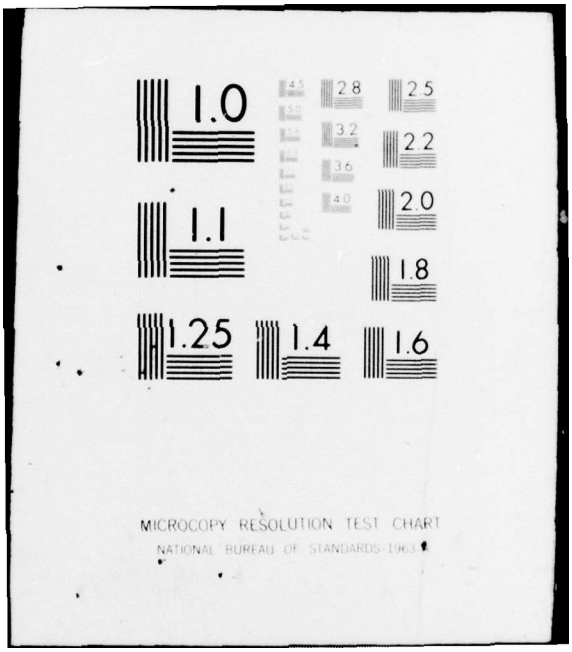
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EFFECT OF OZONE AND CHLORINE ON 3,4-BENZOPYRENE DURING THE DISINFECTION OF WATER

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A number of Soviet and foreign investigators discovered that open bodies of water can be polluted by carcinogenic hydrocarbons, 3,4-benzopyrene in particular. Effluents from by-product coke and shale plants, oil refineries, and gasworks are the most imporatnt sources of pollution by this compound. For example, investigators found 3,4-benzopyrene in concentrations up to 10.9 milligrams/liter in the wastes of a shale plant (P. P. Dikun and A. I. Makhinenko, 1963), up to 3 milligrams/liter in effluent from oil refineries (S. N. Cherkinskiy, et al., 1959), and up to 2.8 milligrams/liter in wastes from a by-product coke plant (Z. P. Fedorenko, 1965). Even purified effluent from these plants generally contains several hundreds of a milligram/liter of 3,4-benzopyrene; in some cases its concentration ranges from 0.3 to 0.6 milligram/liter. The result is pollution of the water by 3,4-benzopyrene (thousandths and sometimes hundredths -- 0.01 to 0.02 -- of a milligram/liter, bottom sediments (from 1.5 to 90 milligrams per 100 grams of ooze), and phytoplankton (from 0.001 to 0.3 milligram/gram).

Z. P. Fedorenko's experiments showed that the tarry substances isolated from sewage possess carcinogenic activity when applied to the skin and that peroral administration to white rats of water containing various concentrations of 3,4-benzopyrene induces malignant and benign tumors of the forestomach. The frequency of tumor development was found to be directly related to the amount of the substance administered.

In the light of the foregoing, it seemed worthwhile to trace the fate of 3,4-benzopyrene dissolved in water and subjected to different kinds of treatment in drinking water supply systems. The subject is inadequately discussed in the literature. There are only a few reports on the effect of chlorination of water on 3,4-benzopyrene dissolved in it. For example, N. N. Trakhtman and M. D. Manita (1966) in a short series of studies found

that at an initial concentration of 1 microgram/liter of 3,4-benzopyrene, 30 minutes after treatment with 0.3 milligram/liter of active chlorine, an average of 0.176 microgram/liter remained in the water and after 2 hours 0.08 microgram/liter of the substance. Following treatment with chlorine at a concentration of 0.5 milligram/liter, an average of 0.188 and 0.006 microgram/liter of 3,4-benzopyrene, respectively, remained after the same periods of time.

Because of the limited information on the subject, we decided to compare the effect of chlorine to that of the most intensive oxidizing agent, ozone, on 3,4-benzopyrene dissolved in water.

Experiments were performed with distilled water or tap water not containing residual chlorine to which a certain amount of 3,4-benzopyrene dissolved in benzene was added. Water was treated with ozone in an experimental apparatus belonging to the Department of Communal Hygiene (the apparatus was described in detail in the collection Voprosy Gigiyeny Naselennykh Mest (Problems of Hygiene of Inhabited Localities), Kiev, Zdorov'ya, 1964, p 44). The apparatus is capable of duplicating natural conditions completely and allows for precise calculation of the amount of ozone actually utilized per liter of treated water. Chlorination was carried out with chlorinated lime according to the chlorine requirement and method of after-chlorination.

3,4-benzopyrene was determined quantitatively before and after the water was treated. The water was treated for this purpose with chemically pure benzene checked for the absence of fluorescence. Extraction was carried out three times by thorough agitation for 15 minutes of a mixture of benzere and water in the ratio of 1:4.

The resulting extract was placed in a Wurtz flask to remove the solvent. The dry residue was dissolved in n-hexane and 3,4-benzopyrene was determined qualitatively from the thin-structure luminescence spectra at the temperature of liquid oxygen (- 183° C). After quantitative identification, the amount of 3,4-benzopyrene was determined by the spectral luminescence method using the photoelectric method of recording the intensities (P. A. Korotkov, N. N. Perzhantova, and V. B. Timofeyev, 1963). The analysis was performed from quasilinear luminescence spectra using 1,12-benzoperylene as an internal standard.

We prepared matrixes of the solutions whose luminescence was excited by a PRK-4 lamp with a UFS-3 filter. The analysis was performed in an ISP-51 spectrograph. An FEU-19 electron photomultiplier supplied by an Orekh stabilizer served as a light detector. A Kaktus microroentgenometer was used to amplify the signal coming from the FEU-19. 3,4-benzopyrene was determined by comparing the intensities at the maximum of the 4021 Å line for 3,4-benzopyrene and 4078 Å for 1,12-benzperylene. The unknown 3,4-benzopyrene concentration was calculated from the relationship:

$$C_x = 0.22\, C_{1,12} \cdot \frac{I_{3,4}}{I_{1,12} - 0.111_{3,4}}$$

The sensitivity of the method is $5 \cdot 10^{-10}$ grams/milliliter.

Study of the effectiveness of chlorination revealed the following. In cases where residual chlorine was in semibound form (as chloramine), the decrease in 3,4-benzopyrene concentration was insignificant. If, however, water free from ammonia (free residual chlorine) was treated with chlorine, the decrease in 3,4-benzopyrene concentration was much greater. For example, when water containing 4 micrograms/liter of benzopyrene was treated with 0.4 to 0.6 milligram/liter, it was found to contain 1 to 1.3 microgram/liter of benzopyrene after 30 minutes, 0.7 to 0.8 microgram/liter after 2 hours, and 0.4 to 0.5 microgram/liter after 24 hours, i.e., it was gradually broken down by the chlorine; the rate of breakdown is described by a logarithmic curve. Increasing the amount of chlorine did not improve the effect of treatment very much. For example, when water containing 4 micrograms/liter of 3,4-benzopyrene was treated with 5 milligrams/liter of chlorine, 0.4 microgram/liter was found after 30 minutes, 0.4 microgram/liter after 2 hours, and about 0.2 microgram/liter after 24 hours. If there was only a little 3,4-benzopyrene (less than 0.5 microgram/liter), small amounts of chlorine completely decontaminated the water within 12 hours.

Graf, et al. (1963), believes on the basis of his research that the products of benzopyrene decomposition after chlorination are 5-monochloro-3,4-benzopyrene (its carcinogenicity has not been studied) and, to a lesser extent, 3,4-benzopyrene -- 5,8-quinone (noncarcinogenic).

Ozonation proved to be more effective, apparently because ozone can break down hydrocarbons with a cyclic structure. For example, after water containing 4 micrograms/liter of 3,4-benzopyrene was treated with 2.5 milligrams/liter of ozone for 3 minutes, it contained only 0.06 microgram/liter of benzopyrene; after it was treated with 4.5 milligrams/liter of ozone for 5 minutes, it contained 0.04 microgram/liter. Even when water was treated with larger amounts of ozone for 10 to 15 minutes, the benzopyrene concentration did not drop below 0.02 microgram/liter. After water containing 0.5 microgram/liter of 3,4-benzopyrene was treated with 2 milligrams/liter of ozone for 3 minutes, the benzopyrene concentration dropped to 0.02 to 0.04 microgram/liter. Further increases in the amount of ozone had little effect. It is reasonable to assume that the benzopyrene fragments formed after ozonization are noncarcinogenic, but this requires direct proof in biological experiments.

Thus, our studies showed that treating water with chlorine or ozone slightly decreases the 3,4-benzopyrene concentration: by a factor of 5 to 10 after chlorination (if free residual chlorine is present in the water) and by a factor of 10 to 50 after ozonization. However, water cannot be completely freed from benzopyrene under practical conditions (after chlorination for .5 to 2 hours or ozonization for 3 to 5 minutes).

Thus, it is extremely important to prevent the pollution of water with 3,4-benzopyrene or other carcinogenic substances by using effective purification methods and to study the effectiveness of removing 3,4-benzopyrene by other methods of treatment.